

Raty et al. generated highly oxygenated organic molecules (HOM) from the ozonolysis of cyclohexene in an environmental chamber. They separately characterized the effects of adding NO and ammonium bisulfate (ABS) seed particles on cyclohexene HOM composition. HOM were detected with a time-of-flight chemical ionization mass spectrometer using nitrate reagent ion. Following NO addition to the chamber, the relative abundance of $C_6H_8O_9$, $C_6H_9NO_9$, $C_{12}H_{19}NO_{11}$ (and other HOM) increased, especially nitrogen-containing HOM. The abundance of $C_6H_8O_7$, $C_{12}H_{20}O_9$ and other HOM decreased. Following ABS addition to the chamber, signals at $C_6H_{10}O_4$, $C_6H_{10}O_6$, and $C_6H_{10}O_8$ – and other low-volatility HOM – decreased due to the increased condensation sink. A model was used to relate the fraction of HOM remaining in the gas phase to its effective saturation concentration (C^*). Overall, the experiments are well motivated from the perspective of trying to better understand (1) the composition of molecules that contribute to new particle formation and (2) the effects of NO_x and condensation sink perturbations on NPF. However, in my opinion, the novelty and atmospheric significance of the results are uncertain the way they are currently presented. The comments below should be implemented into a revised manuscript before I would support eventual publication in ACP.

General Comments

1. Peräkylä et al. (2020) describe a similar set of experiments with a different precursor (α -pinene). In that study, in general, I felt that the analysis was clearer and more thorough than was presented here. At the very least, because a study of cyclohexene-derived HOM is motivated here as “a surrogate for monoterpenes with an endocyclic double bond” to assess “how applicable earlier volatility parameterisations are on the cyclohexene system” a revised manuscript should incorporate parallel analyses to what were presented in the companion Peräkylä et al. (2020) manuscript. For example, Figure 8 in Peräkylä et al. (2020) shows the calculated C^* values of $C_{10}H_{16}O_x$ HOM that were calculated from seed perturbation experiments. Actual C^* values of cyclohexene-derived HOM are never plotted or discussed here as far as I can tell. Also, Figure 7 of Peräkylä et al. (2020) shows a scatter plot comparing the modeled versus measured fraction remaining (FR) of α -pinene-derived HOM. In my opinion this is a much clearer presentation than Figure 8 in this manuscript.
2. After setting up Section 2.3 for a discussion of the cyclohexene ozonolysis mechanism, it transitions to a more abstract/general discussion after L136. I think it would be better to focus the discussion on what happens to the $C_6H_9O_4$ peroxy radical, such as the specific autooxidation and/or RO_2 - RO_2 reactions that lead to some of the major HOM products, i.e. $C_6H_8O_7$, $C_6H_8O_9$, and $C_{12}H_{20}O_9$, which have already been identified in earlier studies (e.g. Rissanen et al.). A figure with a reaction scheme showing these autooxidation steps would also be useful. Reframing the discussion around specific autooxidation steps that lead from $C_6H_9O_4$ to HOM, along with a reaction scheme, allows for a more direct transition to the results and discussion of the NO_x and condensation sink perturbation studies.
3. The way the paper is currently written, the relative roles of $RO_2 + NO$ and $RO_2 + NO_3$ reactions in generating the results that are presented/discussed in Figure 3 and Section 3.1 are not clear: $[NO]$ is below detection limit, and $[NO_3]$ is not constrained by measurements and/or modeling. At the least, a photochemical box model simulation (e.g. KinSim or similar, see Peng and Jimenez, 2019) with the relevant COALA chamber conditions, reactions and rate coefficients would be

appropriate here, perhaps as an appendix. Because the use of cyclohexene is motivated as a simple surrogate for monoterpenes, it would also be appropriate to add another reaction scheme to Section 3.1 that explains the increases or decreases in HOM observed in Figures 3-4 following perturbation by NO (and/or NO₃).

Minor/Technical Comments

4. **L67:** The authors state: “The resulting steady state concentration of ozone was approximately 18 ppb, while a rough estimate for cyclohexene concentration was about 100 ppb [...] estimated from the difference in ozone concentration with and without cyclohexene”. What was the ozone concentration prior to cyclohexene addition? This would be useful for any readers that might try to reproduce the experimental conditions described here. To what extent is the HOM composition, e.g. the monomer:dimer ratio, influenced by [cyclohexene]:[ozone]?
5. **L77:** Please explain why 9 ug/m³ loading of ABS, with corresponding condensation sink of ~0.085 s⁻¹, was chosen for the seed perturbation studies. Additionally, ozonolysis of ~100 ppb cyclohexene presumably generates some SOA given reported SOA mass yields of approximately 0.15 – 0.20 (Keywood et al., 2004). If that’s the case here, what is the condensation sink of homogeneously nucleated cyclohexene ozonolysis SOA relative to the added ABS seeds?
6. Figure 1 and some of the accompanying discussion could probably be moved to an appendix or supplement.
7. Figure 2 and 3 could be combined into a single 2-panel figure to facilitate easier comparison. I would also consider simply adding a 3rd panel showing the mass spectrum of cyclohexene HOM following the addition of 0.085 s⁻¹ ABS condensation sink, and removing Figure 7. Unlike Figure 4, which shows the change in HOM across a continuum of NO_x values, there is only one ABS condensation sink value, so there are no meaningful trends to show in Figure 7 that couldn’t be more simply presented as a mass spectrum to directly compare with Figure 2.
8. Figure 9: I get what the authors are trying to do here, but I find this figure very difficult to read, and as the authors note, quantitatively comparing FR values of cyclohexene and α-pinene HOM is not straightforward because of different SOA loadings and corresponding condensation sinks in the different studies. I suggest removing the α-pinene HOM from this figure, and then adding a separate figure plotting C* values of C₆H₁₀O_x, C₆H₁₀NO_x, C₁₀H₁₆O_x and C₁₀H₁₆NO_x HOM as calculated from the seed perturbation studies.

References

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